

Thermal dissociation of photoproduced excitons at the uv band edge in NaI

W. L. Emkey

Allentown Campus of The Pennsylvania State University, Fogelsville, Pennsylvania 18051

A. B. Romberger

Berks Campus of The Pennsylvania State University, Reading, Pennsylvania 19608

W. J. Van Sciver

Lehigh University, Bethlehem, Pennsylvania 18015

(Received 29 June 1979)

Recombination luminescence is stimulated with red-infrared light in NaI which has been exposed previously to ultraviolet radiation in the low-energy tail of the fundamental absorption spectrum. This stimulated luminescence was undetectable below approximately 65 K and was found to have an activation energy of 0.06 ± 0.01 eV. Evidence is presented which suggests the thermal dissociation of free excitons.

I. INTRODUCTION

When NaI is excited in its fundamental absorption region it exhibits intrinsic luminescence at 4.2 eV.¹ This emission is associated with the radiative annihilation of an electron and a self-trapped hole (V_K center). When the crystal is irradiated at energies greater than the band gap, electrons are elevated to the conduction band, and holes relax into V_K centers. The intrinsic emission results from the capture of the free electron by the V_K center. Excitation at energies below the band gap produces a bound electron-hole pair (free or proper exciton) which may relax into a $\{V_K + e^-\}$ state over a barrier whose activation energy is ~ 0.015 eV.² Meyers and Van Sciver reported the production of isolated V_K centers at temperatures ≥ 78 K in NaI: 10^{-7} Cu resulting from excitation in the low-energy tail of the first fundamental absorption band.³ This discovery resulted from stimulated luminescence experiments whereby red or infrared stimulation yielded intrinsic luminescence after the crystal had been exposed to ultraviolet light at energies below the band-gap energy. This stimulated luminescence appeared as a narrow band in the low-energy tail of the fundamental absorption spectrum. A model was suggested which was based on the Cu^+ impurity acting as a "catalyst" for the production of these free electrons and holes. The work described here reports stimulated-luminescence results over an extended temperature range and on copper-free NaI.

II. EXPERIMENTAL PROCEDURE

The arrangement of the apparatus is shown in Fig. 1. The sample is pre-exposed to uv light

from the deuterium lamp after passing through a monochromator with a 1.7 nm bandpass. When the desired pre-exposure time is reached, the shutter between the monochromator and the deuterium lamp is closed. The crystal then remains in the dark for a period of time referred to as the "dark time." The shutter in front of the tungsten-halogen lamp is then opened, flooding the sample with light which has passed through a filter transmitting light of wavelength $\lambda > 650$ nm. The luminescence stimulated in this manner appears as a short-lived spike on a strip-chart recorder. Information on the time dependence of this spike is limited by the response time of the recording apparatus (≈ 0.5 sec).

The data reported here were taken on NaI samples obtained from two different sources. One set of samples was from the Harshaw Chemical Company (referred to as sample I). These crystals were cleaved from the identical block used in Ref. 3. A second set of samples was of high

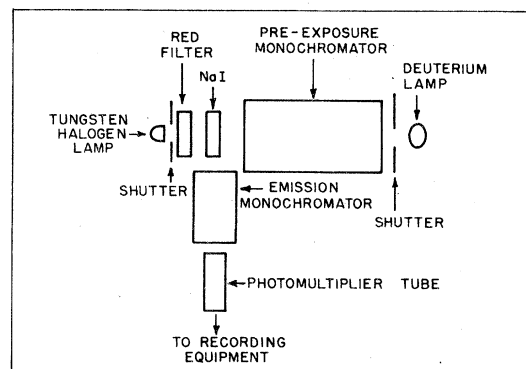


FIG. 1. Experimental arrangement.

purity prepared from zone-refined material at the University of Utah (sample II). Sample I was determined to contain $\sim 8 \times 10^{-8}$ molar fraction copper and $\sim 0.2 \times 10^{-8}$ molar fraction thallium. No copper or thallium was found in sample II, which means $< 10^{-9}$ molar fraction. (Sample II was found to have an emission band at 425 nm. This emission, although close to the Tl emission, was not excited by the characteristic Tl excitation bands. The emission is probably due to some defect in the crystal.)

III. RESULTS AND DISCUSSION

A pre-exposure spectrum is obtained by measuring the stimulated luminescence as a function of the exciting pre-exposure photon energy while keeping both the dark time and the pre-exposure time constant. The pre-exposure spectra for the 4.2 eV emission for sample I at 78 K and 60 K are shown in Fig. 2. It can be seen that when the crystal temperature is lowered sufficiently (below ~ 65 K) the low-energy band becomes undetectable. The corresponding pre-exposure spectra of sample II yield similar results. These spectra are given in Fig. 3.

By assuming a simple exponential dependence of the stimulated luminescence intensity as a function of temperature, i.e., $I = I_0 e^{-\epsilon/kT}$, the activation energy for the low-energy band was determined. The results are shown in Fig. 4. Here a series of stimulated-emission spikes was measured at a given temperature. The data points represent the average value of these spikes. An activation energy of $\epsilon = 0.06 \pm 0.01$ eV is obtained

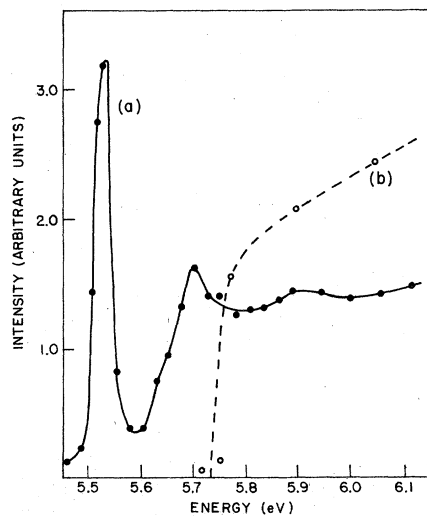


FIG. 2. Pre-exposure spectra for 4.2 eV emission from sample I. (a) 78 K (from Ref. 3), (b) 60 K.

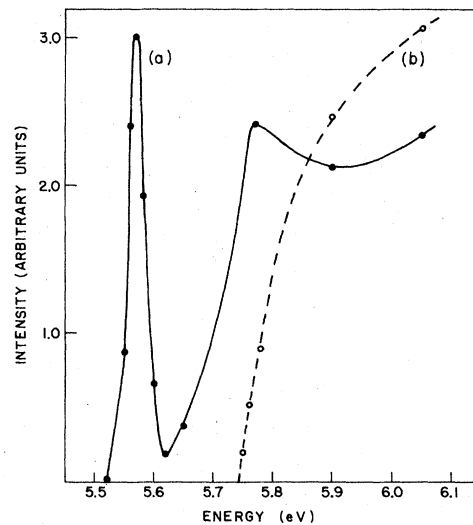


FIG. 3. Pre-exposure spectra for 4.2 eV emission from sample II. (a) 78 K, (b) 60 K.

for both samples I and II.

The intrinsic stimulated luminescence results from freeing a shallowly trapped electron with red-infrared light. The freed electron then recombines radiatively with a V_K center, yielding intrinsic luminescence. In the 80–95 K tempera-

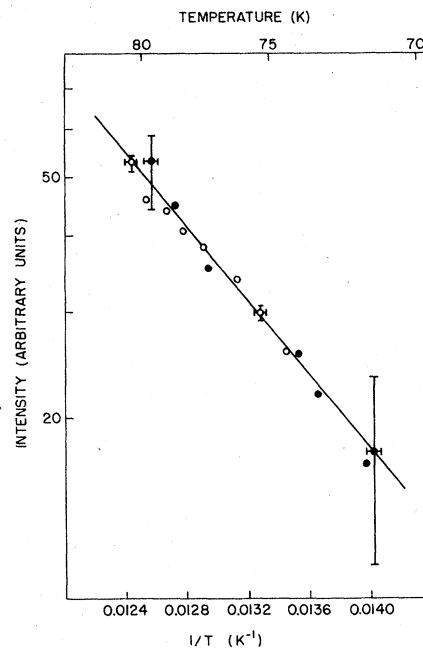


FIG. 4. Intensity of the stimulated luminescence as a function of reciprocal temperature. Pre-exposure at 5.57 eV. ●●● sample I, ○○○ sample II. Representative error bars are indicated.

ture range (Ref. 3), the stimulated intrinsic luminescence decreased as a function of dark time while impurity (Cu^+ and Tl^+) stimulated luminescence increased in a complimentary manner. It was shown that in this temperature region the V_K diffusion-limited activation energy agrees with the activation energy for the diffusion coefficient for V_K centers obtained by Popp and Murray.⁴ Since the V_K center is virtually immobile below ~ 60 K the stimulated luminescence is expected to be independent of the dark time. The results of a dark-time experiment at 40 K are shown in Fig. 5. Aside from a decrease in intensity during the first few seconds, which is probably due to thermal ionization of shallowly trapped electrons, the stimulated luminescence intensity remains constant.

The pre-exposure spectra at 60 K in Figs. 2 and 3 as they relate to the production of V_K centers is understood. Here isolated V_K centers result from a direct excitation of electrons into the conduction band. It should be noted that the threshold energy for the stimulated luminescence in these spectra corresponds to the band-gap energy for NaI. The threshold thus found is in agreement with the band gap as determined by photoconductivity measurements.⁵

Photon energies corresponding to the low-energy tail of the fundamental absorption spectrum of NaI are not sufficient to produce isolated V_K centers directly. The model mentioned in Ref. 3 suggests that the relatively high electron affinity of Cu^+ results in the lowering of the energy required to form a V_K center. This model seems to be inconsistent with the disappearance of the low-energy stimulated-luminescence band at low temperatures. In addition, Figs. 2 and 3 show that the pre-exposure spectra for intrinsic luminescence on the copper-free samples (sample II) are con-

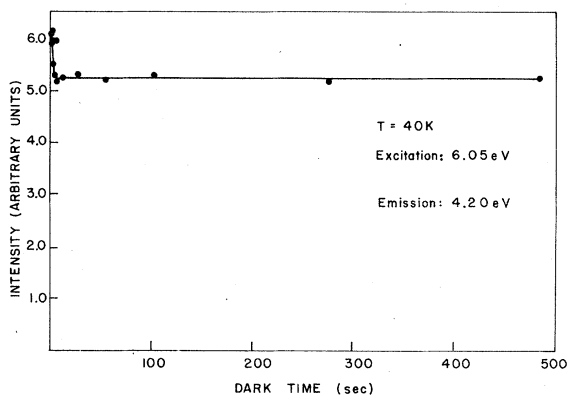


FIG. 5. Intensity of the stimulated luminescence as a function of dark time for sample II.

sistent with the spectra taken on samples containing copper (sample I). Furthermore, the activation energy for the low-energy band shows agreement between samples I and II (Fig. 4). These results not only question the role of Cu^+ in the low-energy photoproduction of V_K centers but also challenge the possible role of any impurity-assisted interaction. The responsible impurity would be identical in both samples and in sufficient concentration to cause the observed effect.

It has been shown that during its finite lifetime the free exciton in the alkali halides can relax into different self-trapped states. Potential barriers have been determined for several of these transitions. As already mentioned, the relaxation of the exciton in NaI to the $\{V_K + e^-\}$ state requires overcoming a 0.015 eV barrier.² This barrier height is consistent with that found by Kuusmann *et al.*⁶ in their study of the edge luminescence in NaI. Emission bands, in addition to the 4.2 eV band, have been observed in NaI.⁷ These emissions are believed to be intrinsic and their behavior is analyzed based upon thermal transitions of the free exciton to different self-trapped emission states. Further, in KI two exciton branching modes have been reported.⁸ The theoretical concept of exciton self-trapping and associated potential barriers has been discussed by others.^{9,10} The analysis of the temperature dependence of the intrinsic luminescence of NaI upon excitation in the exciton region (Ref. 2) predicts that the luminescence efficiency should peak at "LNT (liquid-nitrogen temperature) or above." Instead, the peak occurs at ~ 63 K. It is in this temperature region where the onset of the intrinsic stimulated luminescence appears upon pre-exposure in the exciton region. This behavior is shown in Fig. 6.

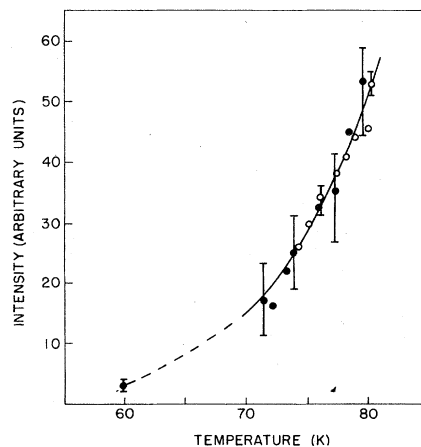


FIG. 6. Stimulated luminescence as a function of temperature. ●●● sample I, ○○○ sample II. (60 K point was determined using $\epsilon = 0.06$ eV.)

The results reported here suggest that a potential barrier of 0.06 eV exists for thermal dissociation of the free exciton in NaI.

IV. CONCLUSION

Excitation in the low-energy tail of the first fundamental absorption band may result in the creation of free electrons and holes. The evidence reported here suggests that this comes about by first creating excitons which are subsequently

thermally dissociated. The role of impurities and/or defects appears to be primarily that of providing shallow electron traps.

V. ACKNOWLEDGMENTS

The authors thank Professor Robert S. Knox for his valuable discussions on this research. We also thank Professor Fritz Lüty for providing us with NaI samples. This research was supported in part by NSF Grant No. DMR 72-03136.

¹W. J. Van Sciver, *Phys. Rev.* **120**, 1193 (1960).

²M. P. Fontana, H. Blume, and W. J. Van Sciver, *Phys. Status Solidi* **29**, 159 (1968).

³P. V. Meyers and W. J. Van Sciver, *Phys. Rev. B* **17**, 4959 (1978).

⁴R. D. Popp and R. B. Murray, *J. Phys. Chem. Solids* **33**, 601 (1972).

⁵W. L. Emkey and W. J. Van Sciver, *Phys. Rev. B* **5**, 610 (1972).

⁶I. L. Kuusmann, Ph. Kh. Liblik, G. G. Liid'ya, N. E.

Lishchik, Ch. B. Lushchik, and T. A. Soovik *Sov. Phys.-Solid State* **7**, 2312 (1976).

⁷H. Nishimura, T. Kubota, and M. Tomura, *J. Phys. Soc. Jpn.* **42**, 175 (1977).

⁸H. Nishimura, *J. Phys. Soc. Jpn.* **38**, 450 (1975).

⁹N. F. Mott and A. M. Stoneham, *J. Phys. C* **10**, 3391 (1977).

¹⁰H. Sumi and Y. Toyozawa, *J. Phys. Soc. Jpn.* **31**, 342 (1971).